

## 4-(4-吡啶基)嘧啶-2-磺酸钠与过渡金属组装的三维氢键网络结构

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**摘要:** 4-(4-吡啶基)嘧啶-2-磺酸钠( $\text{NaL}^2$ )与金属盐( $\text{M}=\text{Mn}, \text{Zn}, \text{Co}, \text{Fe}$ )组装分别得到 4 个配合物, 其分子式为 $[\text{ML}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ 。氢键在这些化合物的超分子结构中起了重要作用。4 种配合物中磺酸基的氧原子没有螯合金属离子, 而是作为氢键的受体, 同时水分子作为氢键给体和受体起到双重作用。另外, 在配合物 **2~4** 中, 杂环上的碳原子也起到供体的作用与磺酸基的氧原子形成氢键。

**关键词:** 组装; 氢键; 4-(4-吡啶基)嘧啶-2-磺酸

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## 3D Hydrogen Bonding Networks Assembled by Sodium 4-(4-pyridinyl)pyrimidine-2-sulfonate with Transitional Metal Salts

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**Abstract:** Sodium 4-(4-pyridin-yl)pyrimidine-2-sulfonate ( $\text{NaL}^2$ ) reacts with metal salts ( $\text{M}=\text{Mn}, \text{Zn}, \text{Co}, \text{Fe}$ ) to form four complexes  $[\text{ML}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$  respectively. Hydrogen bonds play deciding roles in the supramolecular structures. The oxygen atoms of sulfonateo group in four complexes not chelate metal ions but are all involved in hydrogen bonding as the acceptors, while the water molecule plays dual roles both as hydrogen donors and as hydrogen acceptors. Additionally, in complexes **2~4**, the carbon atoms of heterocycles also acted as donor to form hydrogen bonds with oxygen atoms from sulfonateo groups. CCDC: 681493, **1**; 681494, **2**; 681495, **3**; 681496, **4**.

**Key words:** assembly; hydrogen bonding; 4-(4-pyridin-yl)pyrimidine-2-sulfonate

Metal-ligand interactions, hydrogen bonding and  $\pi$ -interactions are very powerful in assembling sophisticated supramolecular architectures which are a topic of considerable interest in recent decades due to their reversibility in direction, selection and formation at room temperature<sup>[1~7]</sup>. Now, hydrogen-bonding interactions are frequently employed as driving forces to give numerous well-defined inorganic, organic and organo-metallic supramolecular architectures<sup>[8~13]</sup>.

Pyridine-2-sulfonate and pyrimidine-2-sulfonate as well as their substituted derivatives have been extensively investigated, which have shown versatile binding patterns to form a variety of coordination polymers and hydrogen-bonded supramolecules with novel structures and properties<sup>[14~16]</sup>.

In previous papers, we reported a multidentate ligand,  $\text{NaL}^1$  together with their metal complexes<sup>[16,17]</sup>. It is noted that the ligand shows an N, N, O-chelation

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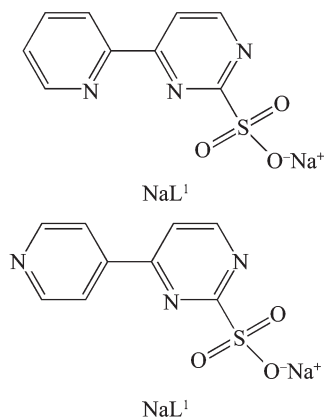
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pattern in the crystal structures of those complexes. As for hydrogen bonds of those complexes, N atoms of pyrimidyl rings and O atoms of the sulfonate groups act as acceptors, while some aromatic C atoms act as donors. Undoubtedly, minor variation of the organic ligand in molecular structure might lead to totally different assembled products and can alter hydrogen-bonding capability in a controlled manner, which provides a handle for fine-tuning supramolecular reactivity. It can reasonably assume that this observation may be translated into a tool that can facilitate practical hydrogen-bonding based on supramolecular synthesis involving a wide range of components.

For a better understanding of the effects involved in the self-assembly process and further investigation of hydrogen bonding based on the pyridinyl-pyrimidine-2-sulfonate ligand, we synthesized a ligand,  $\text{NaL}^2$  (shown in Scheme 1).



Scheme 1 Two types of sodium 4-(pyridinyl)-pyrimidine-2-sulfonates

Herein we report the hydrogen-bonded supramolecules prepared by  $\text{NaL}^2$  with a number of divalent metal ions ( $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ) in formula of  $[\text{ML}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ .

## 1 Experimental

### 1.1 Materials and measurements

All solvents and reagents were of analytical grade and used without further purification. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra ( $4000 \sim 400 \text{ cm}^{-1}$ ) were recorded with a Bruker Vector 22 FTIR spectrophotometer on KBr disks. Electrospray ioniza-

tion (ESI) mass spectra were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of  $100 \sim 1200 \text{ amu}$ .  $^1\text{H}$  NMR spectroscopic measurements were accomplished on a Bruker AM-500 NMR spectrometer, using TMS as an internal reference at room temperature.

### 1.2 Preparation of complexes

#### 1.2.1 Synthesis of $\text{NaL}^2$

Similarly to the literature method<sup>[16]</sup>, ligand was prepared in 10% aqueous NaOH of 4-pyridin-4-yl-pyrimidine-2-thiol (3.76 g, 20 mmol) with 5 equiv of hydrogen peroxide under ice bath. After ten minutes, the solution was warmed for half an hour. Then acetone (50 mL) was added to the solution, pale yellow precipitates were filtered, washed by acetone and dried in vacuo. Yield: 56%.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 500 MHz):  $\delta$  8.90 (d, 1H, pyrimidyl-H), 8.60 (d, 2H, pyridyl-H), 8.05 (d, 1H, pyrimidyl-2), 8.00 (d, 2H, pyridyl-H). ESI-MS  $m/z$  (%)  $-236(100) [\text{L}^2]^-$ . Anal. Calc. for  $\text{C}_9\text{H}_6\text{N}_3\text{SO}_3\text{Na}(\%)$ : C, 41.70; H, 2.33; N, 16.21. Found (%): C, 41.34; H, 2.56; N, 16.22. Main IR absorption (KBr,  $\text{cm}^{-1}$ ): 3 491 (vs), 1 654 (m), 1 576 (s), 1 532 (m), 1 498 (m), 1 436 (m), 1 366 (m), 1 257(s), 1 217(vs), 1 140(s), 1 038(m).

#### 1.2.2 Preparation of complexes $[\text{ML}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ (**1~4**)

The preparation of complexes was identical, and the synthetic process as followed: to a solution of  $\text{NaL}^2$  (0.051 8 g, 0.2 mmol) in warm water (15 mL) was added an aqueous solution (10 mL) of metal salt (0.1 mmol) [**1**:  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ; **2**:  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; **3**:  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; **4**:  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ]. The resulting solution was stirred for 1 hour, cooled to room temperature, filtered, and evaporated slowly to give the single crystals.

$[\text{MnL}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$  (**1**): Yield 81%. Anal. Calc. for  $\text{C}_{18}\text{H}_{22}\text{MnN}_6\text{O}_{11}\text{S}_2(\%)$ : C, 35.01; H, 3.59; N, 13.61. Found (%): C, 35.05; H, 3.55; N, 13.52. Main IR absorption (KBr,  $\text{cm}^{-1}$ ): 3 449 (vs), 1 617 (w), 1 579(s), 1 534(m), 1 432(m), 1 416(m), 1 372(w), 1 249(vs), 1 198 (s), 1 035(s).

$[\text{ZnL}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$  (**2**): Yield 86%. Anal. Calc. for  $\text{C}_{18}\text{H}_{22}\text{ZnN}_6\text{O}_{11}\text{S}_2(\%)$ : C, 34.43; H, 3.53; N, 13.38. Found(%): C, 34.50; H, 3.58; N, 13.15. Main IR absorption (KBr,  $\text{cm}^{-1}$ ): 3 444(s), 1 621(m), 1 573(s), 1 535(m),

1 438(m), 1 367(m), 1 242(s), 1 202(s), 1 041(s).

[CoL<sub>2</sub>·4H<sub>2</sub>O]·2H<sub>2</sub>O (**3**): Yield 83%. Anal. Calc. for C<sub>18</sub>H<sub>22</sub>CoN<sub>6</sub>O<sub>11</sub>S<sub>2</sub> (%): C, 34.79; H, 3.57; N, 13.52. Found(%): C, 35.05; H, 3.67; N, 13.22. Main IR absorption (KBr, cm<sup>-1</sup>): 3 439(m), 1 620(m), 1 573(s), 1 534(m), 1 438(w), 1 368(m), 1 242(s), 1 200(s), 1 041(s).

[FeL<sub>2</sub>·4H<sub>2</sub>O]·2H<sub>2</sub>O (**4**): Yield 72%. Anal. Calc. for C<sub>18</sub>H<sub>22</sub>FeN<sub>6</sub>O<sub>11</sub>S<sub>2</sub> (%): C, 34.96; H, 3.58; N, 13.59. Found(%): C, 35.11; H, 3.47; N, 13.51. Main IR absorption (KBr, cm<sup>-1</sup>): 3 433(m), 1 618(m), 1 576(s), 1 532(m), 1 497(m), 1 384(m), 1 224(s), 1 196(s), 1 042(s).

### 1.3 X-ray crystal structure analysis

Diffraction data for complexes **1~4** were measured at 291 K on a Bruker SMART CCD-1K diffractometer employing graphite-monochromated Mo K $\alpha$  radiation

( $\lambda$  = 0.071 073 nm). The collected data were reduced with the program SAINT<sup>[18]</sup> and empirical absorption correction was done with the SADABS<sup>[19]</sup> program. All the structures were solved by direct methods and refined by full-matrix least squares method on  $F^2_{\text{obs}}$  by using SHELXTL-PC software package<sup>[20]</sup>. All the non-hydrogen atoms were anisotropically refined. The hydrogen atoms were geometrically fixed and allowed to ride on the attached atoms. The summary of the crystal data, experimental details and refinement results for complexes **1~4** are listed in Table 1, selected bond distances and bond angles are given in Table 2.

CCDC: 681493, **1**; 681494, **2**;

681495, **3**; 681496, **4**.

Table 1 Crystal and structure refinement data for complex **1~4**

Complex	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>18</sub> H <sub>24</sub> N <sub>6</sub> O <sub>12</sub> S <sub>2</sub> Mn	C <sub>18</sub> H <sub>24</sub> N <sub>6</sub> O <sub>12</sub> S <sub>2</sub> Zn	C <sub>18</sub> H <sub>24</sub> N <sub>6</sub> O <sub>12</sub> S <sub>2</sub> Co	C <sub>18</sub> H <sub>24</sub> N <sub>6</sub> O <sub>12</sub> S <sub>2</sub> Fe
Formula weight	635.5	646	639.5	636.42
Crystal size / mm	0.5×0.30×0.20	0.4×0.30×0.20	0.3×0.30×0.10	0.3×0.20×0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a$ / nm	0.730 6(3)	0.789 3 (3)	0.786 18(18)	0.783 89(16)
$b$ / nm	1.270 6(4)	1.214 6(4)	1.218 4(3)	1.220 9(3)
$c$ / nm	1.394 5(5)	1.359 4(5)	1.362 6(3)	1.368 0(3)
$\beta$ / (°)	104.094(6)	95.462(7)	95.511(4)	95.382(4)
$V$ / nm <sup>3</sup>	1.256(7)	1.297(8)	1.299(5)	1.303(5)
$Z$	2	2	2	2
$T$ / K	291	291	291	291
$D_c$ / (Mg·m <sup>-3</sup> )	1.681	1.654	1.635	1.622
$\mu$ / mm <sup>-1</sup>	0.767	1.18	0.893	0.811
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
$F(000)$	654	664	658	656
Crystal shape, color	Block, yellow	Block, none	Block, purple	Block, brown
$h_{\min} / h_{\max}$	-8 / 8	-9 / 9	-9 / 9	-9 / 9
$k_{\min} / k_{\max}$	-16 / 11	-14 / 8	-10 / 15	-15 / 11
$l_{\min} / l_{\max}$	-14 / 14	-16 / 16	-16 / 16	-15 / 16
Ref. collected / unique ( $R_{\text{int}}$ )	6 070 / 2 196 (0.058 7)	6 432 / 2 485 (0.052 2)	6 839 / 2 551 (0.030 4)	6 889 / 2 551 (0.046 9)
Observed data [ $I > 2\sigma(I)$ ]	1 884	1 642	2 274	1 847
Parameters	196	187	188	183
Final $R$ [ $I > 2\sigma(I)$ ]	$R_1=0.035$ 2, $wR_2=0.089$ 5	$R_1=0.041$ 4, $wR_2=0.083$ 5	$R_1=0.029$ 7, $wR_2=0.084$ 1	$R_1=0.050$ 8, $wR_2=0.118$ 3
GOF	1.012	0.846	1.077	0.985
Max. and min., $\Delta\rho$ / (e·nm <sup>-3</sup> )	400, -310	490, -340	270, -320	390, -410

$R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ ;  $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$ ,  $w = 1 / [\sigma^2(F_o^2) + (0.050 \ 2P)^2]$  for (**1**) and  $w = 1 / [\sigma^2(F_o^2) + (0.035 \ 4P)^2]$  for (**2**),  $w = 1 / [\sigma^2(F_o^2) + (0.051 \ 2P)^2 + 0.155 \ 6P]$  for (**3**),  $w = 1 / [\sigma^2(F_o^2) + (0.059 \ 1P)^2]$  for (**4**), where  $P = (F_o^2 + 2F_c^2) / 3$ .

Table 2 Selected bond lengths (nm) and angles (°) for complex 1~4

Complexes (M)	1 (Mn)	2 (Zn)	3 (Co)	4 (Fe)
M-O4	0.216 6(2)	0.212 9(2)	0.210 7(2)	0.214 2(3)
M-O5	0.220 4(2)	0.212 6(2)	0.208 7(2)	0.212 4(2)
M-N3	0.227 9(2)	0.211 1(3)	0.213 7(2)	0.218 6(3)
M-O4a	0.216 6(2)	0.212 9(2)	0.210 7(2)	0.214 2(3)
M-O5a	0.220 4(2)	0.212 6(2)	0.208 7(2)	0.212 4(2)
M-N3a	0.227 9(2)	0.211 1(3)	0.213 7(2)	0.218 6(3)
O4-M-O5	89.4(8)	90.2(9)	90.2(6)	91.2(2)
O4-M-N3	93.4(7)	93.1(1)	93.6(6)	93.1(1)
O4-M-O4a	180.0	180.0	180.0	180.0
O4-M-O5a	90.6(8)	89.8(9)	89.7(6)	88.8(1)
O4-M-N3a	86.6(7)	86.9(1)	86.3(6)	86.9(1)
O5-M-N3	89.4(7)	90.6(1)	91.5(6)	90.4(1)
N3-M-N3a	180.0	180.0	180.0	180.0
O5-M-O5a	180.0	180.0	180.0	180.0

Symmetry codes: a: 1:  $-x, 2-y, -z$ ; 2:  $-x, 1-y, 2-z$ ; 3:  $-x, -y, 1-z$ ; 4:  $-x, -y, 2-z$ .

## 2 Results and discussion

### 2.1 Synthesis and general characterizations of $\text{NaL}^2$ and complexes 1~4

Following a literature method<sup>[16]</sup>,  $\text{NaL}^2$  was obtained by oxidation of its precursor (4-pyridin-4-yl-pyrimidine-2-thiol) using  $\text{H}_2\text{O}_2$  as oxidant in a basic condition. It is worthwhile to note that this reaction must be kept under ice bath at first and then should not warm for long time. After those processes acetone should be added to the clear solution to obtain solid-state due to good solubility of pertinent compound in water.

Complex 1~4 were prepared by reaction of metal salts and  $\text{NaL}^2$  in 1:2 molar ratio. Infrared spectra of the four complexes and ligand showed absorption bands resulting from the vibrations of aromatic rings in 1 660~1 300  $\text{cm}^{-1}$  region. Sharp peaks characteristic of the S-O bonds in 1 300~1 100  $\text{cm}^{-1}$  and bands in 1 050~1 000  $\text{cm}^{-1}$  due to  $\nu(\text{C-S})$  were clearly observed<sup>[16]</sup>. In complexes, a band ascribed to coordinated water was shown at 3 500~3 400  $\text{cm}^{-1}$ . Positive ESI-MS spectra in water of  $\text{NaL}^2$  showed predominant peaks centred at  $m/z = 236$ , which was in agreement with the presence of  $[\text{L}^2]^-$ .

### 2.2 Crystal structure of $[\text{ML}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ (1~4)

Complexes 1~4 have the same structure in formula of  $[\text{ML}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ , and the major difference lies in

the nature of metal ions. All the complexes are mononuclear consisting of two anionic ligands and two free water molecules. As the representative one, the molecular structure of complex 1 is shown in Fig.1 with the atom-numbering scheme.

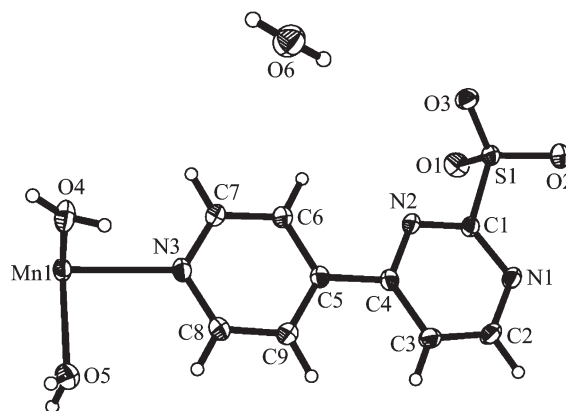


Fig.1 Asymmetric unit of  $[\text{MnL}_2 \cdot 4\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$  showing the numbering scheme and displacement ellipsoids at the 30% probability level

All complexes crystallize in the monoclinic system,  $P2_1/n$  space group and have an octahedral coordinated geometry, which is completed by two pyridyl nitrogen atoms from different ligands and four water molecules. The axial N3-M-N3a bond angles are in the range, ca.  $180^\circ$ . Different from the coordination pattern of  $\text{L}^1$  in previous papers, each  $\text{L}^2$  only acts as unidentate with

nitrogen atom from pyridyl ring. All the bond lengths and angles in complexes **1~4** show normal values. However, it is noted that two heterocyclic rings in each ligand are not coplanar. The dihedral angles between the two heterocyclic rings of four complexes are *ca.* 3.9(3)°, 14.3(8)°, 14.0(5)° and 13.5(2)° respectively.

### 2.3 Structural descriptions of hydrogen-bonded supramolecules

It is noteworthy that the supramolecular formation

of these complexes by hydrogen bonds is very interesting. Sulfonato oxygen atoms, water molecules and aromatic hydrogens of the ligand participate in intermolecular hydrogen bonds, leading to the construction of novel supramolecules. All hydrogen bond patterns are listed in Table 3. Although the actual assembly process may happen all at once rather than stepwise, it is particularly interesting and more convenient to describe the 3D structure formed by

**Table 3** Hydrogen bond geometry for complexes **1~4**

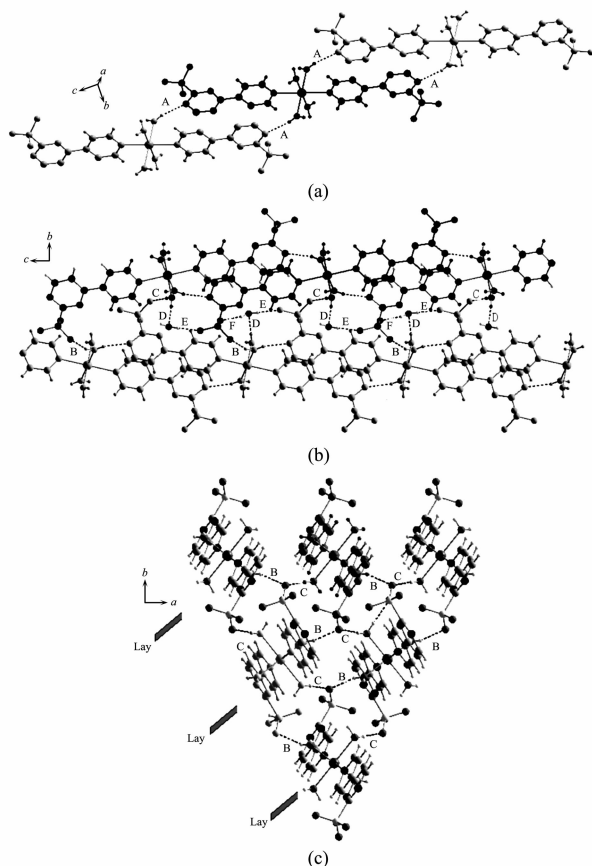
D-H...A	<i>d</i> (H...A) / nm	∠(DHA) / (°)	<i>d</i> (D...A) / nm	Symmetry codes
<b>Complex 1</b>				
A: O4-H...N1	0.21 2(4)	168.0(4)	0.287 5(3)	<i>x, y, -1+z</i>
B: O4-H...O3	0.201 0	159.0	0.278 8(3)	<i>1/2+x, 3/2-y, -1/2+z</i>
C: O5-H...O3	0.208(4)	172.0(4)	0.2887(3)	<i>1/2-x, 1/2+y, 1/2-z</i>
D: O5-H...O6	0.191 0	177.0	0.272 7(3)	<i>-1+x, 1+y, z</i>
E: O6-H...O2	0.196(4)	179.0(5)	0.276 1(3)	<i>1-x, 1-y, 1-z</i>
F: O6-H...O1	0.208(4)	172.0(4)	0.283 3(3)	<i>1/2-x, -1/2+y, 1/2-z</i>
<b>Complex 2</b>				
G: O4-H...O2	0.193 0	169.0	0.274 3(3)	<i>x, -1+y, z</i>
B: O4-H...O3	0.191(4)	170.0(4)	0.272 5(3)	<i>1/2-x, -1/2+y, 3/2-z</i>
C: O5-H...O2	0.239 0	150.0	0.316 0(4)	<i>x, -1+y, z</i>
A: O5-H...N1	0.244 0	124.0	0.300 8(4)	<i>x, -1+y, z</i>
D: O5-H...O6	0.218 0	122.0	0.272 1(4)	<i>1-x, 2-y, 2-z</i>
F: O6-H...O1	0.207 0	151.0	0.284 5(4)	<i>1/2-x, -1/2+y, 3/2-z</i>
E: O6-H...O2	0.214(5)	165.0(5)	0.287 4(4)	<i>x, -1+y, z</i>
H: C2-H...O1	0.246 0	169.0	0.337 7(5)	<i>1/2+x, 5/2-y, 1/2+z</i>
I: C7-H...O3	0.250 0	116.0	0.302 4(4)	<i>1/2-x, -1/2+y, 3/2-z</i>
J: C9-H...O3	0.243 0	145.0	0.324 2(4)	<i>1-x, 2-y, 2-z</i>
<b>Complex 3</b>				
G: O4-H...O2	0.192 0	178.0(2)	0.273 9(2)	<i>x, -1+y, z</i>
B: O4-H...O3	0.199(2)	168.0(2)	0.273 7(2)	<i>1/2-x, -1/2+y, 1/2-z</i>
D: O5-H...O6	0.193(2)	178.0(2)	0.270 7(2)	<i>x, -1+y, z</i>
C: O5-H...O2	0.251 0	144.0	0.320 3(2)	<i>x, -1+y, z</i>
A: O5-H...N1	0.229 0	144.0	0.299 8(2)	<i>x, -1+y, z</i>
F: O6-H...O1	0.208 0	147.0	0.283 3(2)	<i>1/2+x, 3/2-y, 1/2+z</i>
E: O6-H...O2	0.205 0	164.0	0.287 6(2)	<i>1-x, 2-y, 1-z</i>
H: C2-H...O1	0.245 0	169.0	0.336 4(3)	<i>1/2+x, 3/2-y, 1/2+z</i>
J: C9-H...O3	0.243 0	144.0	0.322 9(2)	<i>1-x, 1-y, 1-z</i>
I: C7-H...O3	0.250 0	116.0	0.303 2(2)	<i>1/2-x, -1/2+y, 1/2-z</i>
<b>Complex 4</b>				
B: O4-H4A...O3	0.192(5)	163(5)	0.273 1(4)	<i>1/2-x, -1/2+y, 3/2-z</i>
G: O4-H4B...O2	0.192 0	172.0	0.2739(4)	<i>x, -1+y, z</i>
C: O5-H5A...O2	0.2500	148.0	0.324 9(4)	<i>x, -1+y, z</i>
A: O5-H5C...N1	0.223 0	147.0	0.298 1(4)	<i>x, -1+y, z</i>

Continued Table 3

F: O6-H6B...O1	0.241 0	112.0	0.283 1(4)	$1/2+x, 1/2-y, -1/2+z$
E: O6-H6C...O2	0.207 0	132.0	0.271 0(4)	$x, y, -1+z$
H: C2-H2...O1	0.245 0	170.0	0.337 1(5)	$1/2+x, 3/2-y, 1/2+z$
I: C7-H7...O3	0.249 0	119.0	0.304 4(5)	$1/2-x, -1/2+y, 3/2-z$
J: C9-H9...O3	0.242 0	143.0	0.321 3(5)	$1-x, 1-y, 2-z$

hydrogen bonds in a three-step procedure.

For complex **1**, independent mononuclear units are linked together via heteromeric hydrogen bond A, O4-H...N1, to form a tiled chain. As shown in Fig.2a, hydrogen bonds named A, are involved with cis nitrogen atoms of pyrimidine rings and the hydrogen of coordinated water molecules. On the one hand, the resulted chains are spread through hydrogen bonds, named B, C, D, E and F, parallel to *bc* plane to produce fluctuant 2D hydrogen-bonded layers (Fig.2b). Then the O-H...O interactions, B and C hydrogen bonds, operate between layers in an alternate fashion to give rise to 3D supramolecular network. The coordinated water



(a) 1D chain via hydrogen bonds A; (b) Hydrogen bonds parallel to *bc* plane; (c) Hydrogen bonds B and C parallel to *ab* plane

Fig.2 Hydrogen bonds in complex **1**

molecules as the hydrogen-bonding donor as well as sulfonato oxygen atom O3, take part in forming hydrogen bonds B and C. As for hydrogen bonds F and E, the sulfonato oxygen atoms, O1 and O2, act as acceptors, while O6 of the crystal lattice water, is the donor. Additionally also acting as the acceptor, O6 is involved in hydrogen bond D together with near hydrogen of O5.

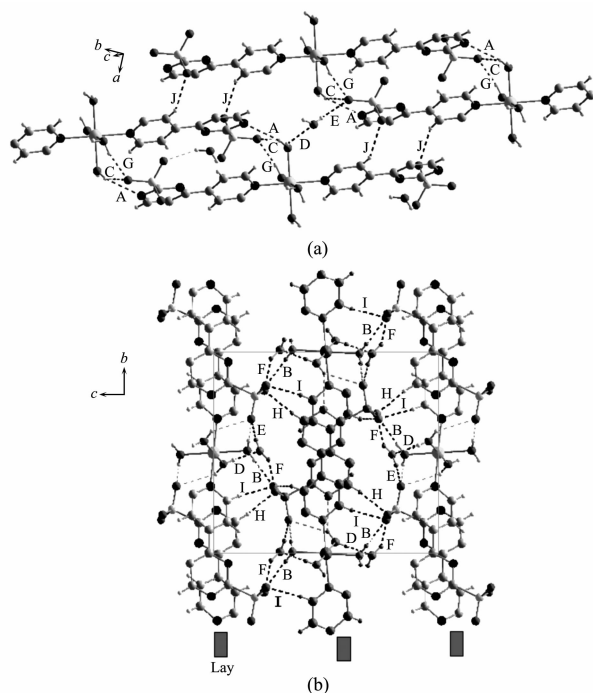
For complex **2**, the hydrogen bonds are more complicated than those of complex **1**. The difference in the crystal packing between **2** and **1** is following. In **2**, the O5-H...N1, O5-H...O2 and O4-H...O2 (named A, C and G respectively) interactions are involved in the forming of infinite tapes. These tapes, in turn, associate further across the parallel edges by hydrogen bonds C9-H...O3, O5-H...O6 and O6-H...O2 (named J, D and E) to make up a corrugated sheet (Fig.3a). The sheets are interconnected through five type hydrogen bonds (named B, E, F, H, I respectively) in *bc* plane (Fig.3b).

In general, in the crystal packing of **2**, heteromeric hydrogen bonds (H, I and J), which play important roles in the crystal packing, are formed by the noncoordinated sulfonato O atoms together with the aryl H atoms in the para position.

For complex **3** and **4**, all hydrogen-bonding patterns are identical with those in complex **2**. Like complexes **1** and **2**, the final assembled structures are 3D hydrogen-bonded architectures.

In summary, compared NaL<sup>1</sup> with NaL<sup>2</sup>, there is just the difference in the N atom position of pyridyl ring. However in the crystal structures of those complexes formed by NaL<sup>1</sup> with metal salts<sup>[16,17]</sup>, L<sup>1</sup> adopts an N, N, O-chelation pattern. As for the latter, L<sup>2</sup> shows unidentate coordination pattern with N atom of pyridyl rings. Meanwhile the hydrogen bonding patterns are also different. There are three types of hydrogen





(a) 2D corrugated plane via hydrogen bonds; (b) Hydrogen bonds parallel to bc plane forming 3D network

Fig.3 Hydrogen bonds in complex 2

bonds in these four supramolecular frameworks,  $\text{O}-\text{H}\cdots\text{N}$ ,  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$ . Three noncoordinated O atoms of sulfonate group and N atom of pyrimidyl rings are just as hydrogen-bonding acceptors. Two water molecules moored to metal ion, acting as the bifurcated donors, donate their H atoms to N and O atoms. It is noteworthy that the typically functions of the free lattice water molecules fixed on the mononuclear unit through intermolecular hydrogen bonds, act as both the donors and the acceptors.

As a result, we have presented herein the structural characterizations of four new mononuclear complexes with  $\text{NaL}^2$ . The use of different substituted groups results in the different supramolecular and crystal structures of these supramolecular complexes. Consequently, simple changes in molecular structure can lead to totally different assembled products and alter hydrogen-bonding patterns.

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